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Semiconductor materials characterisation by Raman spectroscopy

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Abstract Among optical techniques used in the characterization of semiconductors, Raman Spectroscopy (RS) has emerged as a powerful tool. Its advantages are its versatility and well-developed theory which permits the study of phonons, quantitative determination of carrier concentration, stress and electric field besides identification of impurities and unknown phases. It is complementary to the well-known technique of Photoluminescence (PL) and requires similar equipment. RS has also proved to be the most powerful technique for investigating vibrational excitations in superlattices. This paper reviews the application of Raman spectroscopy to semiconductor materials characterisation and provides examples from studies on surface passivation of CdTe, ion-implantation of Si donors in GaAs and evaluation of InGaAs / InP quantum wells

Keywords Raman spectroscopy, semiconductors, quantum wells

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1. Introduction

The discovery of the Raman effect in 1928 [1] besides being a tour de force in fundamental physics provided a new probe for study of materials. Originally applied to the study of liquids and crystals, it has become a tool par excellence in the hand of chemists to study structure and bonding. Raman's original studies on diamond are now classic. Coincidentally silicon and germanium, which are the materials of today's Electronics Revolution both have the diamond structure. III-V compounds such as GaAs crystallize in the related zinc-blende structure while more ionic compounds such as GaN and ZnS have the wurzite structure. First-order Raman scattering from III-V compounds was first reported by Mooradian and Wright [2]. The selection rules for Raman scattering in these crystal classes are well-known and the spectra of a wide range of such compound semiconductors were determined and have been reviewed by Cardona and Guntherodt [3].

Semiconductors are characterised by band gaps which range from ~ 0.1 to ~ 3.5 eV. The measurement of the band gap is best accomplished by optical absorption or photoluminescence (PL) measurements. This is extremely useful for identifying a semiconductor and also for determining the composition of alloys such as $Ga_{1-x}Al_xAs$ where x may be varied during growth according to requirements. PL is also extremely sensitive to the presence of impurities and defects.

With the advent of high power lasers it has become possible to examine monolayer level films, strained layers and quantum wells using Raman Spectroscopy (RS) which has thus come into its own as a tool complementary to PL. Fabrication processes such Ion implantation – annealing also benefit from non-contact evaluation techniques as RS. In this paper some interesting though simple applications of RS will be surveyed and examples given from crystals and quantum structures grown at the author's laboratory at I.I.T Kharagpur, the emphasis being on the materials science aspect. The Raman studies in the last 2 cases were carried out at the National Physical Laboratory, New Delhi.

2. Review

Raman scattering [3] involves the interaction of photons with molecular vibrations or phonons leading to the scattered radiation being shifted in wavelength with respect to the incident radiation. Raman spectra usually plots the intensity of the scattered radiation against the shift in wavelength. Since both energy (frequency) and wave vector are conserved in the scattering process, one-phonon scattering probes only phonons

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at the center of the Brillouin zone. In two-phonon RS there is no restriction in the magnitude of the individual phonon wave-vectors and this can be used to determine the phonon density-of-states. RS which is a second order optical process is also polarization – dependent with selection rules sensitive to the orientation of the crystal surface. Resonant Raman scattering can be used to study interband electronic transitions. However this paper is limited to the discussion of first-order scattering. Some of the properties of semiconductors that can be studied include

a) Crystal orientation [3]

b) Alloy composition and compositional disorder [4]

c) Structural disorder amorphous *vs.* microcrystalline [5, 6]

d) Strain and / or electric field including surface strain due to polish or etch [7, 8]

e) Carrier concentration and depth profiling after ion implantation [9]

g) Microcrystals [10]

h) Presence of oxides / new phases at a surface & interface [11]

The parameters measured in Raman scattering and the information derived there from are summarised in Table 1.

Table 1. Semiconductor properties studied from Raman scattering

No	Measured Parameters	Information
1	Position of LO / TO phonon lines	Material
2	Line shift	Stress, electric field, temperature
3	Line width	Grain size, disorder
4	LO / TO phonon intensity	Crystal orientation, band bending
5	Coupled plasmon / LO phonon modes	Carrier concentration
6	Local modes	Disorder
7	Forbidden modes	Compositional disorder
8	Position of new lines	Alloy composition
9	Spatial variation of intensity	Homogeneity at micron level
10	Variation with incident wavelength	Carrier depth profile
11	Resonant Raman effect	Disorder

3. Experimental results

(i) Surface passivation of CdTe :

CdTe is the most important II-VI compound semiconductor because it can be doped both n & p type and has a direct band gap of 1.54 eV (300K). Thus it is of immense importance for thin film solar cells, as a substrate for HgCdTe IR detectors and also as particle detectors. There is no natural surface passivant for CdTe which is required for reducing surface leakage and increasing minority carrier diffusion lengths.

Studies on photoelectrochemical (PEC) solar cells with CdTe electrodes showed that treatment of the CdTe surface with $RuCl_3$ solution had beneficial effects on both n and p-CdTe surfaces, reducing the surface recombination velocity, increasing minority carrier diffusion lengths and thus solar cell efficiencies [12]. XPS studies [13] showed changes in surface stoichiometry *i.e.* Cd : Te ratio on surface passivation and the formation of a layer of TeO_x ($x = 1.97 - 2.07$). There was no evidence of Ru in-diffusion from SIMS measurements. Raman scattering studies were carried out by Bose and Holtz [14] on unmodified and Ru-modified CdTe surfaces using an Argon ion laser (514.5 nm), a Spex 1403 double monochromator with a cooled GaAs photomultiplier as detector.

The results on unmodified p-CdTe [Figure 1a] showed clear the Raman lines at 140 cm^{-1} and 167 cm^{-1} for TO and LO phonons respectively, together with a weak line at 120 cm^{-1} attributed to

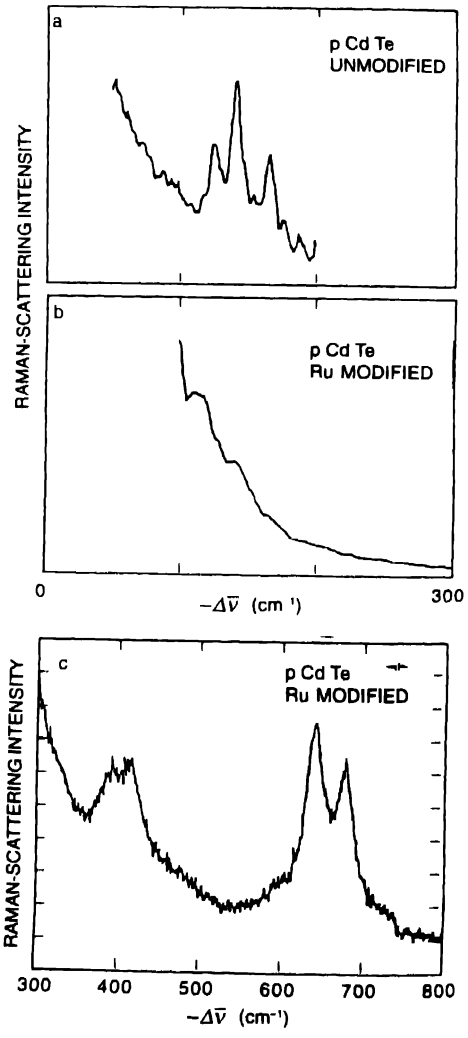

Figure 1. Raman spectra of (a) unmodified p-CdTe, (b) Ru modified p-CdTe (0 – 300 cm^{-1}) and (c) Ru modified p-CdTe (300–800 cm^{-1})

ystalline Te. Ru- modified p-CdTe showed strong lines at 393, 14 641 and 678 cm^{-1} and weak peaks at 460 and 596 cm^{-1} igure 1b, 1c]. While the line at 678 cm^{-1} can be identified with $dTeO_3$, the other lines correspond very well with those bserved for bulk single crystal TeO_2. The presence of $CdTeO_3$ suggested from the Cd–Te–O phase diagram. The results on CdTe were very similar. These results permitted the conclusion at

i) unmodified CdTe had a thin overlayer of Te with no oxide

ii) Ru treatment resulted in the dissolution of Cd in the alkaline electrolyte and

iii) the conversion of Te into TeO_2 with Ru acting as a catalyst,

iv) there was no evidence of the formation of any Ru compound

TeO_2 is known to be a wide band gap semiconductor which ovides a window layer for CdTe (as does AlGaAs on GaAs) nd also terminates dangling bonds thus passivating the CdTe urface. Such unambiguous evidence about the species present n CdTe surfaces is not forthcoming through any other available echnique

ii) Si implantation & annealing in GaAs :

fabrication of GaAs MESFETS involves the implantation of donors typically Si into semi-insulating (SI) GaAs. The energy of the implant determines the penetration depth of the Si while the dose determines the carrier concentration. Since the implant process causes severe lattice damage, this must be followed by annealing for a suitable time and at a suitable temperature. This process also activates the implanted Si *i.e.* converts un-ionised impurities into substitutional donors giving the required free electron concentration. The two implants carried out for source-rain and channel formation respectively were as follows :

$\times 10^{13}/cm^2$ at 35 KeV and ii) $5.45 \times 10^{12}/cm^2$ at 150 KeV.

ic annealing process is usually optimised by simulation nd by resistivity and Hall measurements on implanted-nnealed samples [15]. This is a somewhat time-consuming rocess as it involves the formation of electrical contacts on the amples. Raman spectroscopy provides an elegant contact-free olution to the determination of the free carrier concentration n $(N_D - N_A)$. This is obviously less than the concentration of mplanted Si due to the presence of un-ionized impurities.

has been shown that in a semiconductor such as GaAs ving a carrier concentration $n > 2 \times 10^{17}/cm^3$, the longitudinal ical (LO) and acoustical (LA) phonon modes couple with e carriers to form 2 branches L_+ and L_- of plasmon-phonon ies [9]. The frequency of the L_+ mode starting from ω_1 varies $^{1/2}$ and tends asymptotically towards the plasma frequency $_p$ while the frequency of the L_- mode tends asymptotically wards ω_t of the TO mode.

Raman scattering studies [Figure 2(a-c)] carried out on three such samples with identical implant conditions but different annealing conditions are given in Table 2. The observed L_+ and L_- frequencies and carried concentrations deduced from the

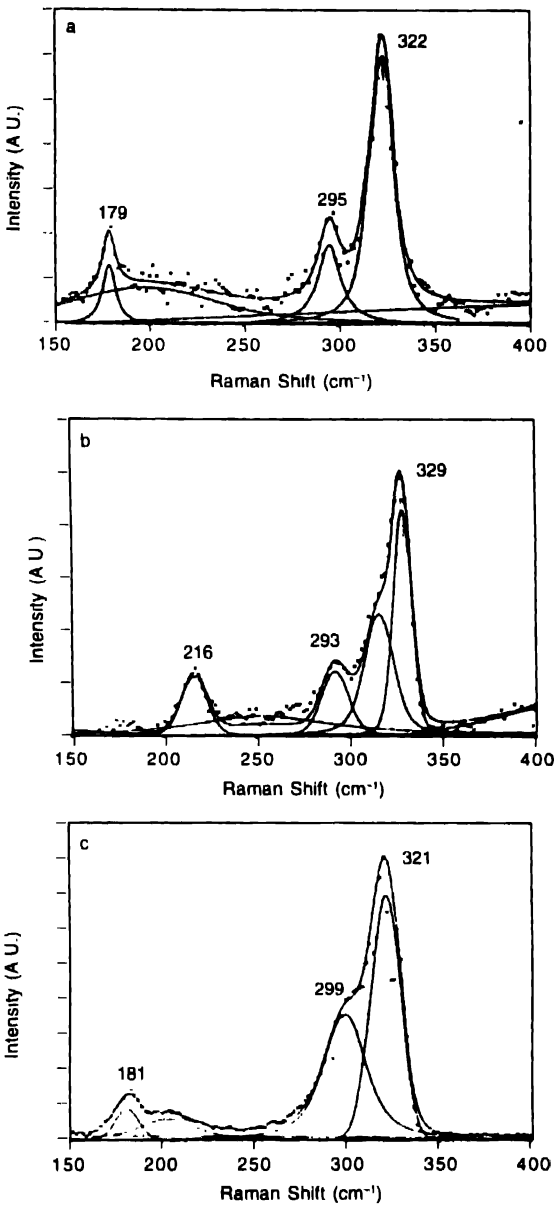

Figure 2. Raman spectra of si–implanted GaAs (a) Sample 1 – unnealed at 900°C, 25 s, (b) Sample 2– annealed at 925°C, 15 s and (c) Sample 3 – annealed at 950° C, 6 s.

plasmon-phonon dispersion curves are shown. These are compared with carrier concentrations deduced from Hall measurements. It is clearly seen that sample 2 gives the highest free carrier concentration in excellent agreement with Hall measurements which gives the surface carrier concentration N_s/cm^2.

The simplicity and elegance of the Raman measurements is thus evident. It has been further shown by Holtz *et al* [10] that using lasers of different wavelengths (457.9 nm – 799.3 nm),

Table 2. Raman studies on Si implanted and annealed GaAs.

Sample	Anneal condition	L_- (cm^{-1})	L_+ (cm^{-1})	N/cm^3 (× 10^{18}) (Raman)	N_S / cm^2 (× 10^{13}) (Hall)
1	900 C, 25 s	322	295, 179	4.5	1.26
2	**925 C, 15 s**	**329**	**293, 216**	**6.3**	**1.42**
3	950 C, 6 s	321	299, 181	5.0	1.34

which have penetration depths varying by an order of magnitude in GaAs, it is possible to probe the carrier concentration at different depths. This provides valuable information otherwise obtainable only by electro-chemical profiling or by Secondary Ion Mass Spectrometry (SIMS) which are both destructive processes. Further SIMS gives the total and not the ionized impurity concentration

(iii) InGaAs / InP heterojunctions and quantum wells :

For the analysis of thin semiconductor layers, heterostructures and quantum wells Raman spectroscopy is widely used because of its sensitivity down to monolayer thickness and ability to obtain information non-destructively from nm to microns below the surface.

$In_{1-x}Ga_xAs$ ($x = 0.47$) is an important alloy that can be grown lattice-matched on InP. It has a direct bandgap of 0.75 eV (300 K) which makes it ideal for detectors in fibreoptic communication at 1.55 μm. $In_{1-x}Ga_xAs$ quantum wells with InP barriers are now extensively used as laser sources.

RS has been used to probe the phonon structure in these layers as described in detail by Yu and Cardona [17]. Davey *et al* [18] had studied InGaAs / InP multiquantum wells with well widths of 10 nm and barrier widths of 10 nm and 3 nm in two different samples having 10 and 50 periods. The Raman spectra showed weak peaks due to folded LA phonons between 60 – 150 cm^{-1} with a periodicity of 14 cm^{-1}. This corresponded to a bilayer (well + barrier) widths of 20 nm and 13 nm for the 2 samples.

For the present studies $In_{1-x}Ga_xAs$ ($x = 0.47$) quantum wells of width 2.5, 3.9, 7.8 and 15 nm were grown by MOVPE in a Thomas Swan reactor at 550° C on an (100) n-InP substrate. The barrier widths were 15 nm. Raman spectra were obtained using an Argon ion laser with a single monochromator and a photon counting detector. The spectra showed strong peaks at 329 cm^{-1} characteristic of LO phonons in InP and a slightly smaller peak at 293 cm^{-1} for LO phonons in InGaAs. This latter peak is slightly shifted from the bulk value indicating the presence of strain.

The spectra due to zone-folded LA phonons shown in Figures 3a and b are remarkably sharp and strong for a structure containing only 4 periods compared with 10 and 50 periods used by Davey *et al*. Strong peaks for InP and InGaAs are present but in addition a periodic set of peaks are observed below 150 cm^{-1} in Figure 4b. The values of peak shift are 91.69, 105.35, 118.28, 133.89 with a separation of 13 cm^{-1} approx. These can be attributed as scattering due to folded LA phonons present in a multiquantum well structure with an average bilayer width of 23.5 nm.

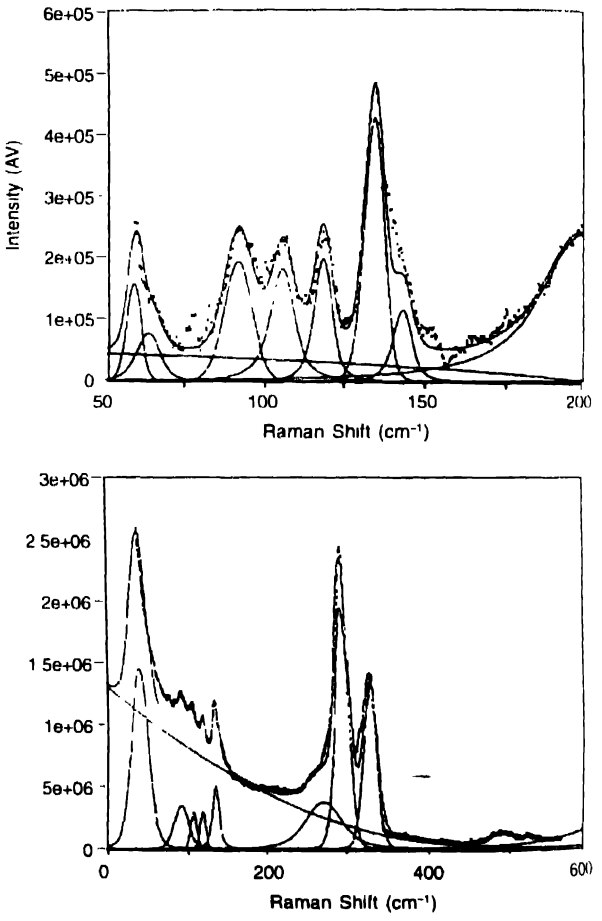

Figure 3. Raman spectra of InGaAs / InP quantum wells (a) showing InGaAs and InP phonon lines (0–600 cm^{-1}) and (b) showing zone-folded acoustic phonons (0–200 cm^{-1}).

Theoretically the spacing has been shown to be inverse proportional to the superlattice period. Hence such spectra enables the determination of the superlattice period. The results are in good agreement with the results of Double Crystal X-ray Diffraction (DXRD) which gave a bilayer width of 25.2 nm. while PL emission peak from QW structures give information about the well width, Raman spectra provide complen

information about the superlattice period *i.e.* bilayer width = width of well + width of barrier. Close examination of the spectra also show the presence of interface modes due to InAs, GaP layers that may form between well and barrier.

4. Conclusion

The paper provides some examples of the use of Raman Spectroscopy in examining the surface passivation of semiconductors, in the determination of carrier concentration due to ion implantation and the bilayer width in multiquantum well structures The advantages are the non-destructive nature and comparative simplicity of the measurements compared with alternative techniques such as electrochemical profiling, SIMS and TEM measurements.

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